INTERLABORATORY STUDY 98-1

PETROLEUM HYDROCARBONS IN SOIL

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PETROLEUM HYDROCARBONS IN SOIL

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INTERLABORATORY STUDY 98-1: PETROLEUM HYDROCARBONS IN SOIL

1 INTRODUCTION

Total Petroleum Hydrocarbon (TPH) content in soils is recognized as an important parameter in the assessment and restoration of contaminated sites across Canada. In certain provinces, it is suspected that excess TPH in the ground, leads to contamination of ground-water and affects the 'wetability' of soils causing problems for vegetation.

A number of private laboratories and government agencies have contributed TPH analytical data that are used in the assessment of contaminated sites. The methods employed for analysis and the carbon fractions used in computations vary from one laboratory to another and from one jurisdiction to another. This has led to high interlaboratory variability and poor data comparability. The interlaboratory study conducted by the Canadian Association for Environmental Analytical Laboratories (CAEAL) in 1997 confirms this high variability between laboratories and analytical methods[1].

With the support those Ontario private laboratories belonging to International Association for Environmental Testing Laboratories (IAETL), the Laboratory Services Branch (LSB) of the Ontario Ministry of the Environment, reviewed the performance of Ontario participating laboratories in the above CAEAL study [2]. As a follow-up of this review process, the LSB undertook the present TPH interlaboratory study to determine whether there has been some improvement in interlaboratory variability following the CAEAL study and to possibly identify causes that may lead to this variability.

2 STUDY INFORMATION

A letter of invitation was sent to several Ontario laboratories with fifteen laboratories agreeing to participate in this study. A copy of the letter of invitation is included in Appendix 1. The study samples along with the results reporting sheets and a methodology questionnaire (Appendix 2) were dispatched on September 23, 1998.

The study samples consisted of three soils. Samples 1 and 2 were provided by the Water Technology International Corporation(WTI), Burlington, Ontario. These samples were used in a previous study conducted by the Canadian Association for Environmental Analytical Laboratories (CAEAL). Sample 3 was provided by LSB. All three soil samples were dried, milled, sieved, and fortified with varying amounts of petroleum products and throughly mixed. Details of sample production and preparation protocols are available from respective agencies.

Each participant was asked to analyze all three samples following the methodology outline provided with the letter of invitation. Laboratories that opted to do additional analyses with variation from the prescribed method were encouraged to do so and report those results separately. All laboratories were required to submit information requested in the methodology questionnaire.

Once received by the LSB, the final reported results were entered onto an electronic spreadsheet. The responses to the methodology questionnaire were entered into a database and a copy of the results spreadsheet was faxed to each participant to verify the accuracy of transcription.

3 RESULTS

Of the fifteen laboratories agreeing to participate results were received from 12 laboratories (80%). The participant list is provided in Appendix 4. Two laboratories confirmed with LSB that they were unable to perform the analysis at this time. Four laboratories reported results using more than one method. Results from each method are treated as a separate laboratory and are identified by suffix A and B, following their laboratory identity code (LABID).

The results are presented in Table 1. The `positive results' i.e. those not reported as `less than' (<) are also presented in the form of bar charts in Figures 1 and 3 and 5. The responses to the methodology questionnaire are summarized in Tables AP1 to AP4 (Appendix 3).

TABLE 1
RESULTS AS REPORTED

	SAMPLE 1				SAMPLE 2				SAMPLE 3			
LABID	C5-10 ug/g	C10-C24 ug/g	C24-C50 ug/g	HEAVY OILS ug/g	C5-10 ug/g	C10-C24 ug/g	C24-C50 ug/g	HEAVY OILS ug/g	C5-10 ug/g	C10-C24 ug/g	C24-C50 ug/g	HEAVY OILS ug/g
98101	100	370	102	300	28	400	104	270	<0.5	180	1250	1500
98102	135	415		240	33	270		185		25		1200
98103	41	387	63	<100	<10	260	78	<100	45	30	1260	1150
98104	130	310	30	200	60	230	<20	200	10	30	180	900
98104A	180	340	20	200	60	270	20	200	<10	20	170	900
98105	81	535		<100	38	344		<100	<0.1	68		1060
98106	140	106	<	160	98	91	<	<100	<	<	45	1020
98106A	200	248	<	740	120	158	<	750	na	12	18	1670
98106B				<100				410				1120
98107	197	624.5	<20	<500	83.7	357	<20	<500	<10	<10	<20	<500
98107A	365				154							
98109	14.6	208	19.2	38	5.41	206	18.5	57	0.1	48.5	1390	975
98110		378	<100	380		162	<100	430		44	1410	1690
98110A	74.4				9				1.5			
98110B	96.1				3.15				<1			
98112	240	515	70	70	95	394	83	<20	<0.2	51	1070	540
98113	160	280	<mdl	200	78	190	mdl	220	<mdl	22	1000	1060
98114	55	nd	925	980	32	nd	1668	1700	nd	nd	1460	1460

4 EVALUATION

The results from the four fractions of the three samples are presented in Table 1. Each column represents results from all of the laboratories for individual fractions of each sample. **Only `positive results' i.e. those not reported as `less than' (<) were included in any of the following computation and/or evaluation.**

Firstly, mean, median, standard deviation(SD) and coefficient of variance(CV), of all positive results (identified with suffix `all'), were computed for each column. They are presented in Tables 2,4,6 and 7. Then Dixon Outlier Test[3] was performed for each column and the corresponding means, medians, SDs and CVs were computed for the data remaining after Dixon's elimination process. These are identified by the suffix `selected'. Eliminated data points are identified in red in these tables.

Further evaluation of the data was performed by the MOE-LSB K-S technique[4]. This diagnostic technique uses the Youden's concept[5] of considering two samples at a time where the result of one sample is plotted against the result of the other sample (see Figure 2) . Each point represents the pair of data from a single participant. The graph is divided into four quadrants by two lines representing the median value of each sample. In the absence of any systematic error, the results will randomly spread between the four quadrants. Also, if the test samples were heterogeneous, one would expect results to be equally distributed among the four quadrants as each of the following combinations will have same probability of occurrence:

high in sample 1, high in sample 2
high in sample 1, low in sample 2
low in sample 1, high in sample 2
low in sample 1, low in sample 2

When the majority of the results are distributed in the lower left hand and upper right hand quadrants, it is reasonable to conclude that the samples are homogeneous.

The evaluation is based on the median and standard deviation (SD) of the two samples. When results were eliminated by Dixon's process, median and standard deviations of the remaining results are used, otherwise, the median and standard deviation of all the results are used.

It is customary to draw a circle with the point of intersection of the median lines as center and some factor times within-run standard deviation as the radius. This circle represents acceptance limits where 95 % of the laboratories are expected to lie if there are no systemic errors among them. However, in this study, due to the high variability of the data, two times between laboratory standard deviation (SD) was arbitrarily chosen as the radius for drawing the acceptance limit boundaries. When the SD for both samples are not significantly different as determined by the F-test, they are pooled to obtain the appropriate standard deviation. When this is the case, the results are plotted in absolute scale (Figure 2, 4A, and 6A). However, when the SD for both samples are significantly different as determined by the F-test, it is necessary to plot the results in relative scale (Figure 4B and 6B). The results are plotted as percentage of the appropriate median and the CV's are pooled to get the appropriate standard deviation.

FIGURE 1: LIGHT FRACTION

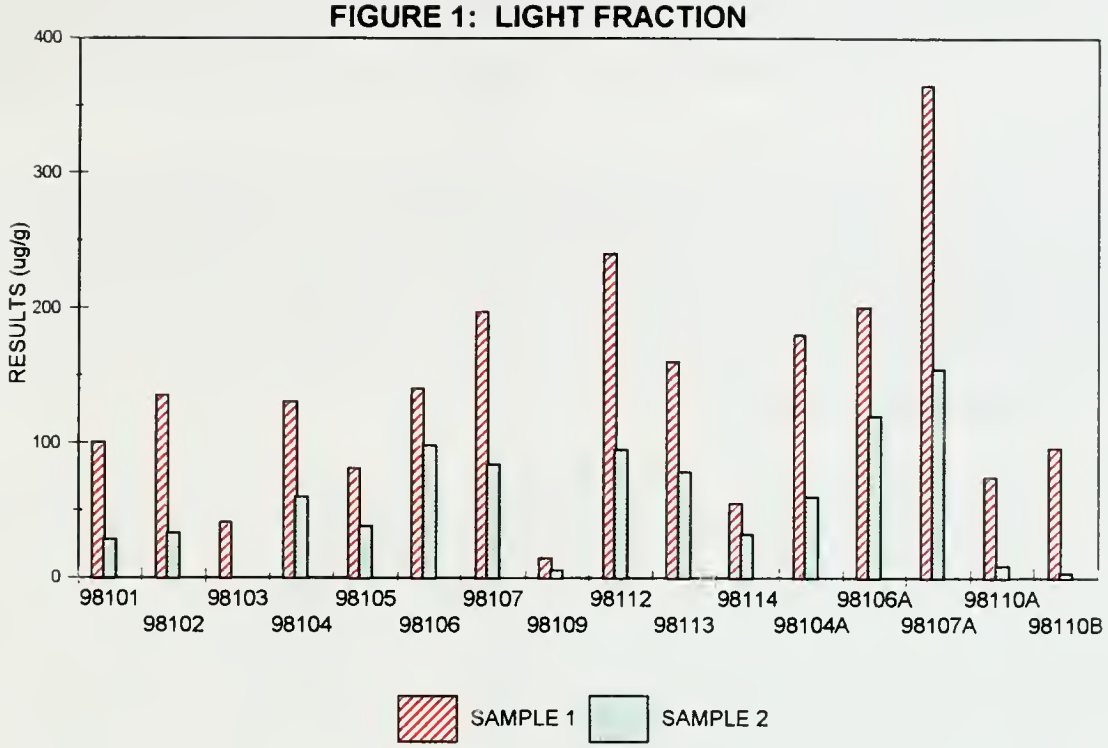
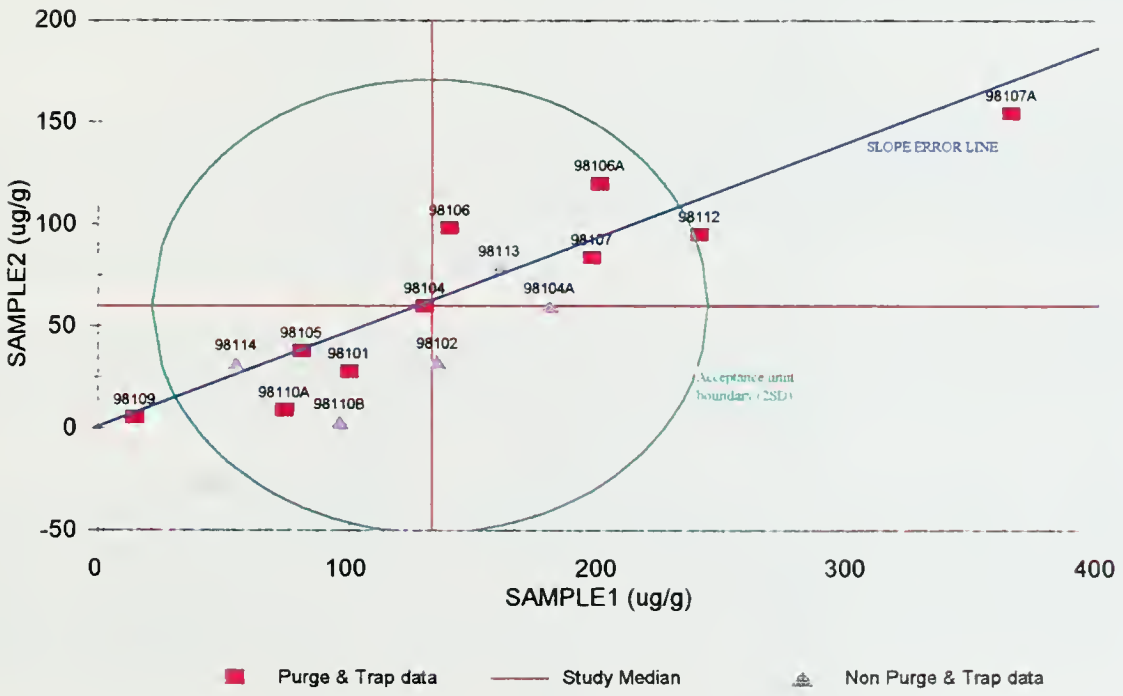


FIGURE 2 : LIGHT FRACTION

K-S PLOT: SAMPLE 1 VS SAMPLE 2



Even though the acceptance boundary was drawn using the equation of the circle ($X^2+Y^2=R^2$), it will appear as an ellipse in the diagrams as the x-axis and y-axis in these plots are not necessarily in the same scale. Thus, the participants that appear within this ellipse are to be considered as performing satisfactorily based on the median and between laboratory variability of all the selected laboratories

A blue line is drawn such that it passes through the origin and the point of intersection of the two median lines, representing a slope or proportional error. Laboratories that exhibit deviation from the median that is concentration-dependant will appear close to this line. Slope errors are usually attributed to biases caused by calibration problems and or inadequacies of the method such as incomplete extraction.

4.1 LIGHT FRACTION (C5-C10)

TABLE 2
LIGHT FRACTION RESULTS

Note: Data in red typeface are those eliminated by Dixon Test

LABID	SAMPLE 1	SAMPLE 2
	ug/g	ug/g
98101	100	28
98102	135	33
98103	41	
98104	130	60
98104A	180	60
98105	81	38
98106	140	98
98106A	200	120
98107	197	83.65
98107A	365	154.5
98109	14.6	5.41
98110A	74.4	9
98110B	96.1	3.15
98112	240	95
98113	160	78
98114	55	32
n	16	15
SD_{all}	84.3	43.1
$mean_{all}$	138.1	59.8
CV_{all}	61.0%	72.0%
$median_{all}$	132.5	60
$SD_{selected}$	62.5	
$mean_{selected}$	122.9	
$CV_{selected}$	50.9%	
$median_{selected}$	132.5	

Sixteen light fraction results from twelve laboratories were reported for samples 1 and 2. Sample 3 results were reported by only four laboratories. Sample 3, by design, was not expected to contain any light fraction, so no further evaluation was performed with the Sample 3 results. The data point eliminated by Dixon's process is identified in red typeface in Table 2.

The K-S plot for the light fraction (Figure 2) shows that all of the results are either in the lower left or upper right quadrants indicating that systematic errors were the major contributors to the between-laboratory variability. It can also be concluded that the samples are homogenous . The results can be distinguished on the basis of the instrumentation employed. Laboratories using the purge and trap methodology are identified by red rectangles and the others are identified by purple triangles. Of the sixteen sets reported, ten were by use of purge and trap-MS, three were by use of head space-FID and the remainders were by use of other methods. The results of laboratory 98103 are not represented in this graph as they provided positive results for only Sample 1.

Of the results submitted thirteen appeared within the acceptance limits determined by the median and between laboratory variability. Seven pairs of results including the one that is right on the point of intersection of median lines (98104, 98105, 98107, 98107A, 98109, 98113, 98114), appear close to the blue slope error line. These laboratories, while showing excellent within laboratory precision, show biases with respect to each other and the study median. These biases appear to be the major contributor to the overall between laboratory variability. The differences between the calibration standards used by different participants could be considered as a probable cause for these biases. This point is clearly illustrated by laboratory 98107 where two different calibration standards (d8-toluene and C7-C10 paraffins) were used while employing the same instrumental methodology, produced results (98107 and 98107A) that lie far apart on this blue line.

Five pairs of results (98101, 98106A , 98110A , 98110B and 98112) appeared slightly away from the blue line indicating that both imprecision and biases described above have contributed to the deviation from the study medians.

Three other pairs of results (98102, 98104A and 98106) appeared close to one of the median lines which indicates that one of their results was close to the median value while the other was some distance away. This is usually indicative of erratic behavior. It must be noted that even though these three participants demonstrated imprecision, their results compared to the majority of the participants, were close to the two medians.

This study has shown that most participants showed good reproducibility. The difference among them is caused by differences in the calibration process including uncertainty of the standards used and/or differences in the methods employed.

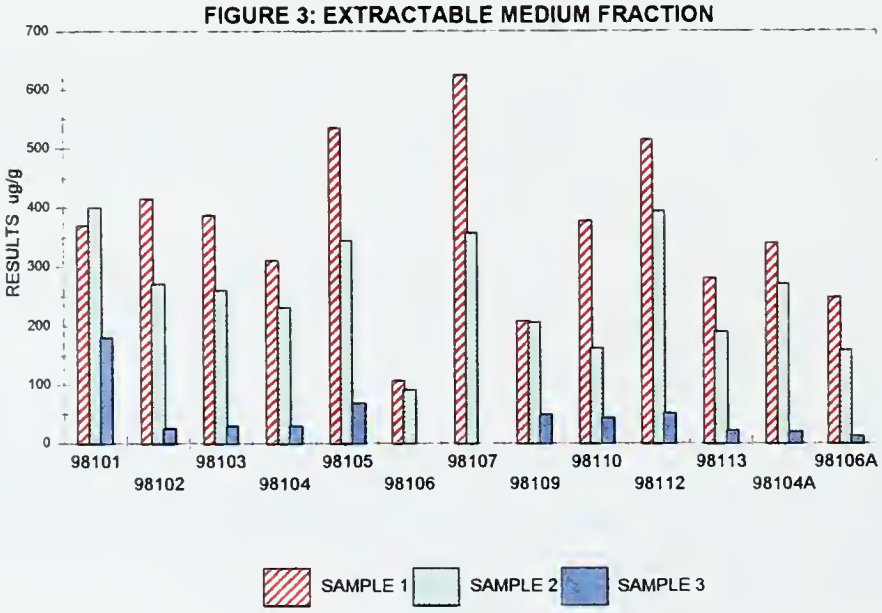
Seven laboratories that participated in the present study also participated in the previous CAEAL study. A performance comparison for the light fraction using the same samples (Sample 1 and Sample 2) is presented in Table 3. It can be observed that the interlaboratory variability as indicated by CV, is reduced by a factor of 2 in the present study. It is also noted that the mean value for Sample 2 in both studies is more or less the same indicating that the light petroleum fraction (C5-C10) present in Sample 2 has remained stable over one year.

TABLE 3
SUMMARY OF STATISTICS FOR LIGHT FRACTION RESULTS

		CAEAL STUDY	MOE 98-1
SAMPLE 1	Mean	315.2 ug/g	164.6 ug/g
	Standard deviation	188.2 ug/g	42.51 ug/g
	CV	59.7%	25.8%
	Maximum	670 ug/g	240 ug/g
	Minimum	96.1 ug/g	100 ug/g
	Range	573.9 ug/g	140 ug/g
SAMPLE 2	Mean	75.0 ug/g	68.0 ug/g
	Standard deviation	57.4 ug/g	26.4 ug/g
	CV	76.5%	38.8%
	Maximum	170 ug/g	98 ug/g
	Minimum	33.6 ug/g	28 ug/g
	Range	136.4 ug/g	70 ug/g

4.2 EXTRACTABLE MEDIUM FRACTION (C10-C24)

FIGURE 3: EXTRACTABLE MEDIUM FRACTION



Thirteen results were reported extractable medium fraction for samples 1 and 2. Eleven results were reported for Sample 3. The data point eliminated by Dixon's process is identified in red typeface in Table 4.

TABLE 4
EXTRACTABLE MEDIUM FRACTION RESULTS

Note: Data in red typeface are those eliminated by Dixon Test

LABID	SAMPLE 1 ug/g	SAMPLE 2 ug/g	SAMPLE 3 ug/g
98101	370	400	180
98102	415	270	25
98103	387	260	30
98104	310	230	30
98104A	340	270	20
98105	535	344	68
98106	106	91	
98106A	248	158	12
98107	624.5	357	
98109	208	206	48.5
98110	378	162	44
98112	515	394	51
98113	280	190	22
n	13	13	11
SD_{all}	135.4	92.5	44.4
$mean_{all}$	362.8	256.3	48.2
CV_{all}	37.3%	36.1%	92.3%
$median_{all}$	370	260	30
$SD_{selected}$			16.3
$mean_{selected}$			35.1
$CV_{selected}$			46.7%
$median_{selected}$			30

The K-S technique was applied to two pairs of data namely Sample 1 versus Sample 2 (Figure 4A) and Sample 1 versus Sample 3 (Figure 4B) . Figure 4A is in absolute scale and Figure 4B is in relative scale.

The majority of data points, as in the case of light fraction, are distributed in the lower left and upper right quadrants in the two plots indicating that systematic error is very prevalent and that there is no evidence of sample inhomogeneity.

In the first case (Sample 1 vs Sample 2; Figure 4A), eleven of the thirteen pairs of results were within the acceptable limits determined by the median and between-laboratory variability. Nine pairs of results (98102, 98103, 98104, 98104A, 98105, 98106, 98106A, 98112 and 98113) appear close to the blue slope error line indicating excellent within-laboratory precision. Their differences can be largely attributed to inter-laboratory biases. In the second plot (Sample 1 vs Sample 3), all of the results appeared within the acceptance limits, but the laboratories tend to show a greater level of imprecision.

FIGURE 4A: EXTRACTABLE MEDIUM FRACTION

K-S PLOT: SAMPLE 1 VS SAMPLE 2

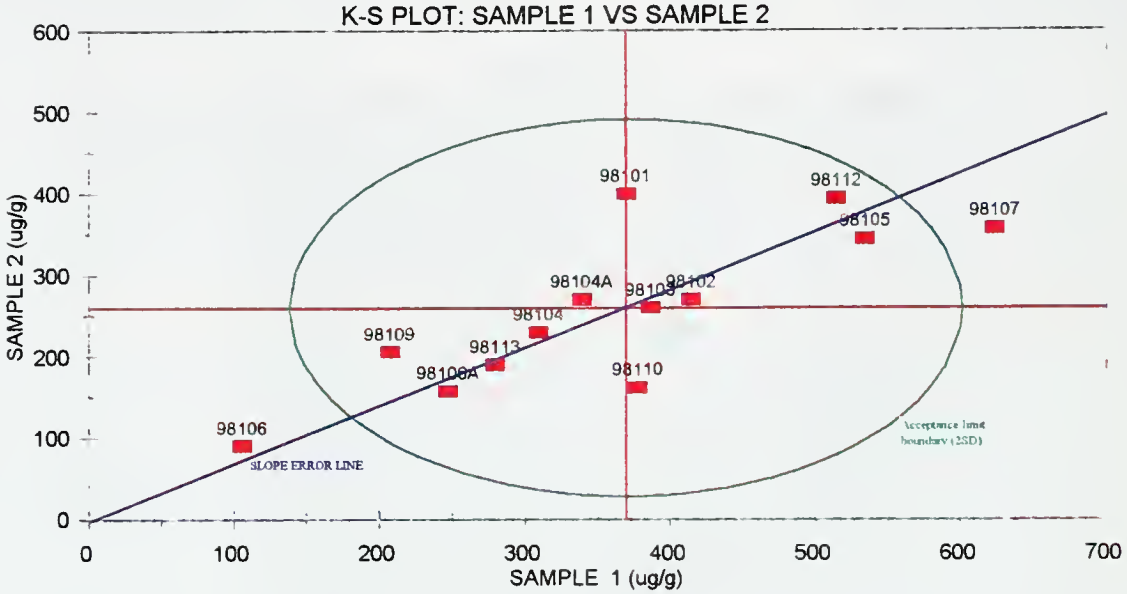
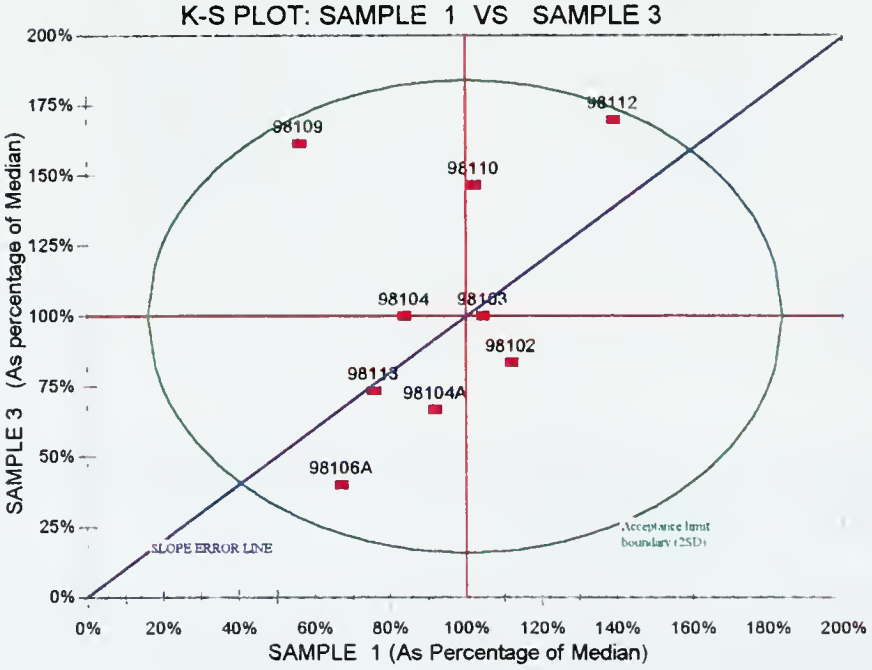


FIGURE 4B:EXTRACTABLE MEDIUM FRACTION

K-S PLOT: SAMPLE 1 VS SAMPLE 3



As in the case of light fraction, the overall variability among the laboratories can be attributed to differences in calibration process including uncertainties of the standards employed and/or differences in the methods employed. Even though all participants used GC/FID , differences in the extraction solvent used, sample clean-up procedure used, analytical column used and injection process (see Tables AP2 and AP3 in the Appendix 3). may have contributed considerably to the bias observed among each other.

Seven laboratories from the present study also reported results for the extractable medium fraction in the previous CAEAL study [2]. A performance comparison between the two studies using the same samples (Sample 1 and Sample 2) is presented in Table 5. It is observed that the interlaboratory variability as indicated by CV, has not improved in the present study. It must be noted that the mean values of results in both studies is more or less the same indicating that the medium petroleum fraction (C10-C24) present in both samples have remained stable over one year.

TABLE 5
SUMMARY OF STATISTICS FOR EXTRACTABLE MEDIUM FRACTION RESULTS

		CAEAL STUDY	MOE 98-1
SAMPLE 1	Mean	366.6 ug/g	378.6 ug/g
	Standard deviation	98.3 ug/g	153.9 ug/g
	CV	26.8%	40.7%
	Maximum	475.0 ug/g	624.5 ug/g
	Minimum	165 ug/g	106 ug/g
	Range	310 ug/g	518.5 ug/g
SAMPLE 2	Mean	247.6 ug/g	281.7 ug/g
	Standard deviation	51.0 ug/g	105.1 ug/g
	CV	20.6%	37.3 %
	Maximum	320 ug/g	400 ug/g
	Minimum	91 ug/g	91 ug/g
	Range	229 ug/g	309 ug/g

4.3 HEAVY OILS (GRAVIMETRIC)

Eleven, ten and fourteen results were reported for heavy oils (gravimetric) for sample 1 , 2 and 3 respectively. The date points eliminated by Dixon's process are identified in red tytpeface in Table 6.

The K-S technique was applied to two pairs of data, namely, Sample 1 versus Sample 2 (Figure 6A) and Sample 1 versus Sample 3 (Figure 6B). Figure 6A is in absolute scale and Figure 6B is in relative scale.

As seen in the previous cases, the majority of data points are distributed in the lower left and upper right quadrants in the two plots indicating that systematic error is very prevalent and that the samples are homogeneous.

TABLE 6
HEAVY OILS (GRAVIMETRIC) RESULTS
Note: Data in red typeface are those eliminated by Dixon Test

LABID	SAMPLE 1 ug/g	SAMPLE 2 ug/g	SAMPLE 3 ug/g
98101	300	270	1500
98102	240	185	1200
98103			1150
98104	200	200	900
98104A	200	200	900
98105			1060
98106	160		1020
98106A	740	750	1670
98106B		410	1120
98109	38	57	975
98110	380	430	1690
98112	70		540
98113	200	220	1060
98114	980	1700	1460
n	11	10	14
SD_{all}	275.2	457	309.8
$mean_{all}$	318.9	442.2	1160.4
CV_{all}	86.3%	103.3%	26.7%
$median_{all}$	200	245	1090
$SD_{selected}$	99.3	114.9	
$mean_{selected}$	198.7	246.5	
$CV_{selected}$	50%	46.6%	
$median_{selected}$	200	210	

FIGURE 5: HEAVY OILS (GRAVIMETRIC)

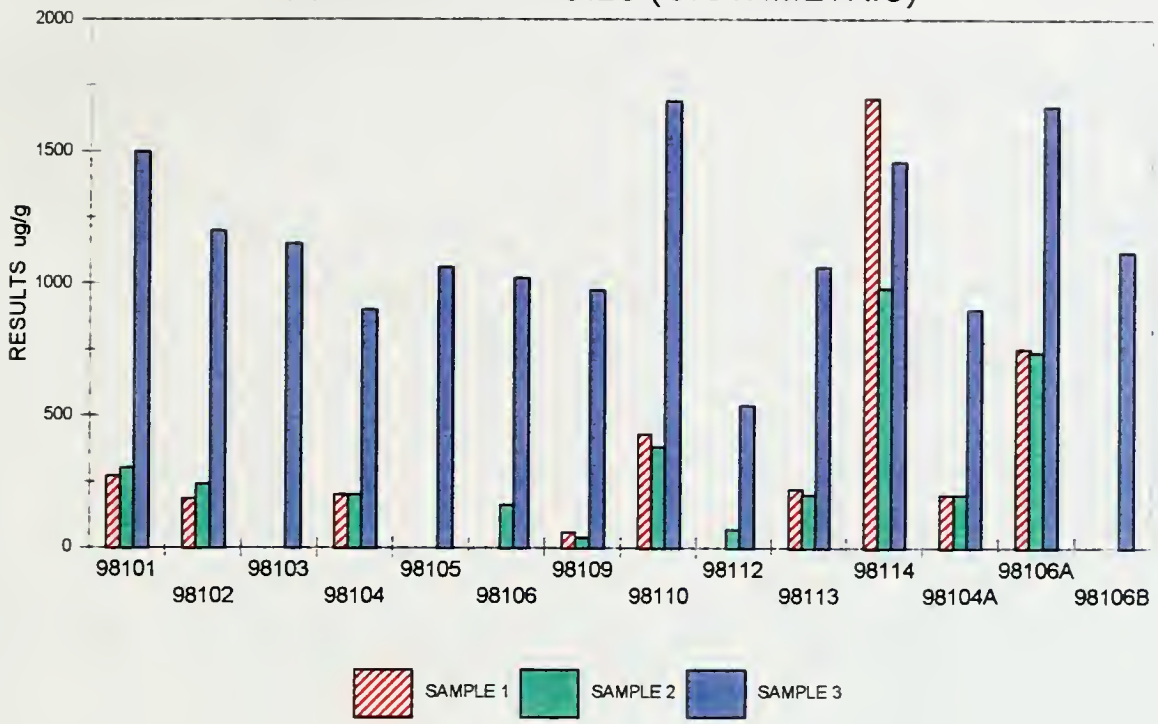


FIGURE 6A: HEAVY OILS (GRAVIMETRIC)

K-S PLOT: SAMPLE 1 VS SAMPLE 2

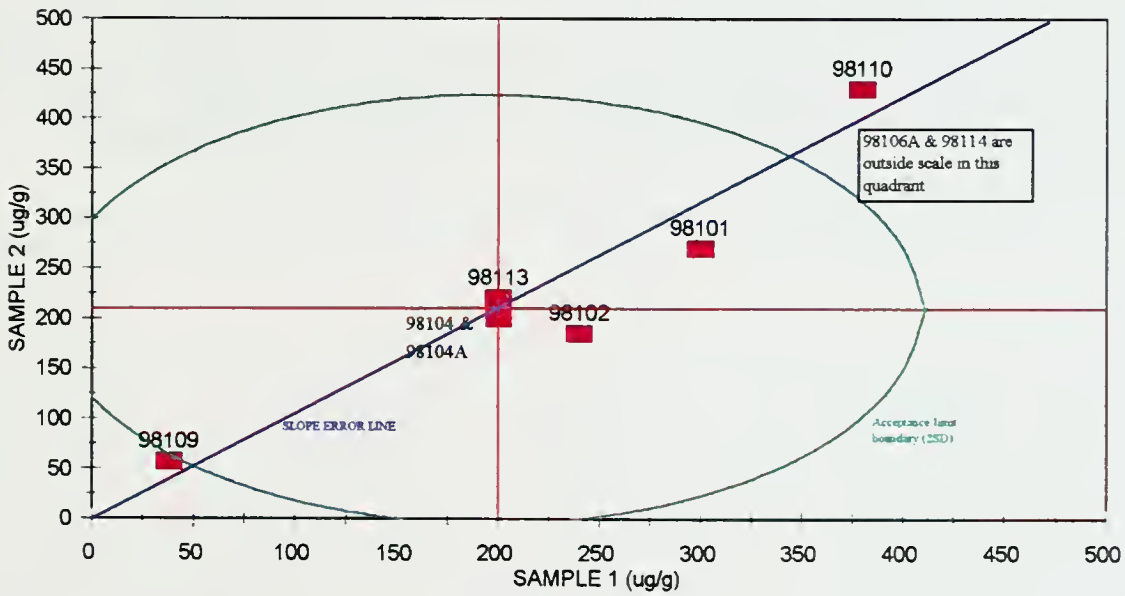
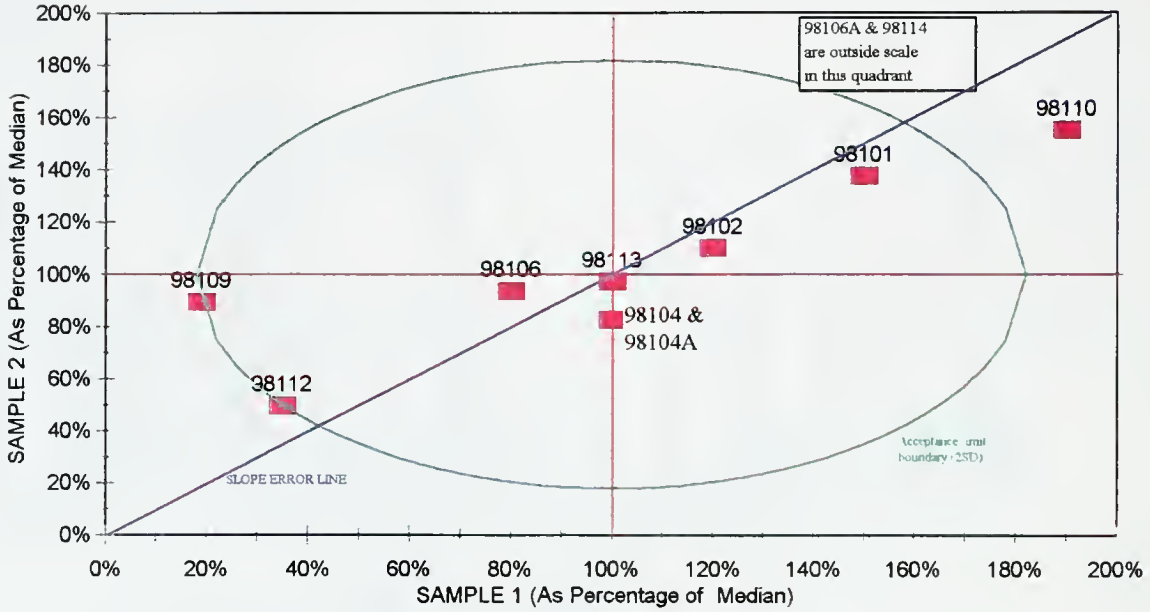


FIGURE 6B: HEAVY OILS (GRAVIMETRIC)

K-S PLOT: SAMPLE 1 VERSUS SAMPLE 3



In the first K-S Plot (Sample 1 vs Sample 2; Figure 6A), five of the nine pairs of results (98101, 98102, 98104, 98104A and 98113), are within acceptable limits based on the median and between-laboratory standard deviation. The others appeared either in the lower left hand or upper right hand quadrants. In the second plot (Sample 1 vs Sample 3), eight of the eleven pairs of results were with in the acceptable limits. The remaining three appear in the upper right hand quadrant. These diagrams indicate that most of the laboratories exhibited good within-laboratory precision and that systematic errors were the major contributors to the overall analytical variability.

4.4 EXTRACTABLE HEAVY FRACTION (C24-C50)

Seven, five and eleven participants reported extractable heavy fraction results for samples 1 , 2 and 3 respectively. The date points eliminated by Dixon's process are identified in red in Table 7

TABLE 7
EXTRACTABLE HEAVY FRACTION RESULTS
Note: Data in red typeface are those eliminated by Dixon Test

LABID	SAMPLE 1 ug/g	SAMPLE 2 ug/g	SAMPLE 3 ug/g
98101	102	104	1250
98103	63	78	1260
98104	30		180
98104A	20		170
98106			45
98106A			18
98109	19.2	18.5	1390
98110			1410
98112	70	83	1070
98113			1000
98114	925	1668	1460
n	7	5	11
SD_{all}	307.2	639	574
$mean_{all}$	175.6	390.3	841.1
CV_{all}	174.9%	163.8%	68.3%
$median_{all}$	63	83	1070
$SD_{selected}$	30.3	31.8	
$mean_{selected}$	50.7	70.875	
$CV_{selected}$	59.8%	44.8%	
$median_{selected}$	46.5	81	

As there were only limited pairs of data available for this fraction, K-S analysis was not performed.

5. CONCLUSIONS AND RECOMMENDATIONS

The single most powerful conclusion that can be drawn from this study by the application of the K-S diagnostic technique [4], is that, most laboratories are capable of very precise analysis. In other words, repeatability or within-laboratory precision is good. The difference among them is predominantly due to individual biases. Even when the same instrumental technique is applied, slight variations in sample preparation seems to contribute to these biases. In some cases, the differences are caused by the different calibration standards and techniques employed.

Another conclusion is that the samples used in this study are homogeneous. Samples 1 and 2 have been used in the previous CAEAL national study[1,5]. A review of the means and standard deviations of all the results in these two studies (Table 8) show that Samples 1 and 2, supplied by WTI, have remained stable over a period of one year. These materials will therefore constitute a useful ongoing quality control material for routine use by laboratories.

TABLE 8
SUMMARY OF STATISTICS OF TWO STUDIES
(all positive results included)

Sample	Study	Light Fraction C5- C10			Medium Fraction C10-C24		
		n	Mean	Standard deviation	n	Mean	Standard deviation
Sample 1	CAEAL	31	249	124.5	25	412	123.5
	MOE 98-1	16	138.1	84.3	13	362.8	135.4
Sample 2	CAEAL	31	70	35	25	267	80.0
	MOE 98-1	15	59.8	43.1	13	256.3	92.5

If reduction of interlaboratory variability and improved data comparability is the goal, Ontario laboratories must strive to develop a 'consensus method' that will meet data quality objectives. This study suggests that it is not sufficient enough to describe the sample preparation and instrument/calibration techniques in general terms and that perhaps finer detail must be prescribed and strictly adhered to by participating laboratories. Further more, standardization of calibration standards used by contributing laboratories against a common reference standard will significantly reduce the interlaboratory variability.

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APPENDIX 1

LETTER OF INVITATION

RE: INTERLABORATORY STUDY 98-1, PETROLEUM HYDROCARBONS IN SOIL

You are invited to participate in Interlaboratory Study 98-1, Petroleum Hydrocarbons in Soil. Laboratory Services Branch (LSB) of the Ontario Ministry of the Environment (MOE) is proposing amendments to the "Light: Extractables" component of the analysis for Total Petroleum Hydrocarbons in soil, as outlined in the MOE document, *Guidance on Sampling and Analytical Methods for Use at Contaminated Sites in Ontario, Revised December 1996*, ISBN 0-7778-5908-4, PIBS 3516E. This interlaboratory study is being conducted to establish the between-laboratory variability using the proposed amended method, as well as comparability to the gravimetric method outlined in the above guidance document.

The methodology that LSB is proposing has been established in LSB Method E3397A. Copies of this method have been made available to Ontario members of the International Association of Environmental Testing Laboratories (IAETL). Ontario laboratories that are not members of IAETL but who wish to participate in this study, may obtain a copy of this method from LSB, by contacting Sheri Teresi at (416) 235-6311.

Laboratories that wish to participate in this study **MUST** follow the criteria outlined in Table 1, attached to this letter of invitation. The required methodology information has been extracted from the MOE guidance document, Table 8.3.2, and Method E3397A.

Laboratories who participate in this study and wish to provide additional results from alternate methods, may do so. A brief summary of the alternate method(s) must be provided with the data.

Study Design

This study will consist of three (3) soil samples to be provided to each participant. Participants will receive approximately 40 g of soil per sample. Participants will be asked to analyze the samples in duplicate, using the criteria provided in Table 1. Results are to be reported for the following fractions: Light Hydrocarbons (C5 - C10) using a GC method, Medium (C10 - C24) using the specified Extraction/GC method, Heavy (C24 - C50) using the specified Extraction/GC method, and Heavy using a Gravimetric method. A questionnaire regarding methodology will be provided with the report form and samples.

Samples will be shipped the **Week of August 24, 1998**.

Results will be due by **October 2, 1998**.

An interim report will be available within 3-4 weeks after all results have been received. A final report will be released subsequently.

Please indicate your interest in participating by returning the attached response form by **August 21, 1998**.

Sincerely,

Sylvia Cussion
Laboratory Quality Audit Scientist
(416) 235-5842
FAX: (416) 235-6312
e-mail: cussiosy@ene.gov.on.ca

TABLE 1
INTERLABORATORY STUDY 98-1
ANALYTICAL GUIDELINES AND METHOD DETECTION LIMITS (MDLs)

Target Parameters	Carbon Range	MDL for Soils & Sediments	Method Guidelines
Light: Sum of Total Purgeables	C5 - C10	10 μg/g	**Sample Preparation:** An aliquot of soil is weighed directly into a purge vessel. VOC-free water and minimum of three surrogates are added to the purge vessel. **Instrumental Measurement:** Heated purge & trap and GC/MS or GC/FID. Quantitate relative to toluene. Headspace-GC/MS or GC/FID technique may be applied.
Light: Sum of Extractables Changed to - Medium: C10 - C24 and Heavy: C24- C50	C10 - C50	10 μg/g 10 μg/g 20 μg/g	**Sample Preparation:** An aliquot is extracted by microwave (Soxhlet or ultrasonic are acceptable alternates) extraction with hexane/acetone (1:1). Extracted is back-extracted with Pure Water to transfer polar compounds into water/acetone fraction. The hexane faction is passed through a 24 cm column of activated 60/200 mesh silica gel, using 40% DCM/hexane. **Instrumental Measurement:** Analysis by GC/MS or GC/FID and quantification by integrating total area in which the C10-C50 compounds are eluted. For the C10-C24 range, it is recommended to quantitate to relative to C16. For the C24-C50 range, it is recommended to quantitate relative to C36. If a different n-alkane is used, it must be specified. Recommended GC column: OV-1ht, 30 m X 0.32 mm X 0.25 μm, 100% dimethyl gum **OR** DB-1ht, 30 m X 0.25 mm X 0.1 μm **Reporting**: Report C10 - C24 and C24 - C50.
Heavy Oils (Extractables)		100 μg/g	A hexane/acetone (1:1) extract (soxhlet, microwave or ultrasonic) is fractionated using silica gel (as for extractables above) , dried and analyzed gravimetrically.

NOTE: Contact Sheri Teresi at (416) 235-3611 for a copy of LSB Method E3397A, if required.

INTERLABORATORY STUDY 98-1
PETROLEUM HYDROCARBONS IN SOIL

YES, I will participate in Interlaboratory Study 98-1 ☐

NO, I will not be participating in Interlaboratory Study 98-1 ☐

Laboratory Name: _____

Contact Person: _____

Telephone: _____

FAX: _____

Shipping Address: _____

_____

_____

_____

Return by **August 21, 1998** to:

Sylvia Cussion
FAX: (416) 235-6312
MOE, LSB, QMU, 125 Resources Rd.
Etobicoke, Ont., M9P 3V6
e-mail: cussiosy@ene.gov.on.ca

APPENDIX 2

RESULTS REPORT FORM
AND
METHODOLOGY QUESTIONNAIRE

INTERLABORATORY STUDY 98-1
PETROLEUM HYDROCARBONS IN SOIL

REPORT FORM

DUE DATE: OCTOBER 30, 1998

Sample No.	Carbon Range	MDL	Units	Result	Comments
1	Light: C5-C10				
	Extractable Medium: C10-C24				
	Extractable Heavy: C24-C50				
	Heavy Oils Gravimetric				
2	Light: C5-C10				
	Extractable Medium: C10-C24				
	Extractable Heavy: C24-C50				
	Heavy Oils Gravimetric				
3	Light: C5-C10				
	Extractable Medium: C10-C24				
	Extractable Heavy: C24-C50				
	Heavy Oils Gravimetric				

INTERLABORATORY STUDY 98-1
PETROLEUM HYDROCARBONS IN SOIL

METHODOLOGY QUESTIONNAIRE

Please complete the following regarding the analysis of the three soil samples provided for Interlaboratory Study 98-1. If you have provided results using two different methodologies, please indicate clearly the differences between the methods and to which set of results the different methods apply.

6. Sample Preparation

a) Light: C5-C10

Weight of soil: _____

Sample Pretreatment: _____

b) Extractables (Medium C10-C24 and Heavy C24-C50)

Weight of soil: _____

Extraction Technique (please circle): Microwave Soxhlet Ultrasonic

Other (please specify) _____

Extraction Solvent: Hexane/Acetone(1:1) Other _____

Back extraction (Pure Water): Yes No

Clean-up column: 24 cm 60/200 mesh silica gel Yes No

Other (please specify): _____

Clean-up solvent: 40% DCM/hexane Yes No

Other (please specify): _____

c) Heavy Oils (Gravimetric)

Weight of soil: _____

Extraction Vessel: Tube Beaker Aluminum Dish

Other: _____

Extraction Technique (please circle): Microwave Soxhlet Ultrasonic

Other (please specify) _____

Extraction Solvent: Hexane/Acetone(1:1) Other _____

Back extraction (Pure Water): Yes No

Sample blowdown: Yes No

Please describe: _____

Clean-up column: 24 cm 60/200 mesh silica gel Yes No

Other (please specify): _____

Clean-up solvent: 40% DCM/hexane Yes No

Other (please specify): _____

Drying Temperature: Dryness in fumehood; followed by 30 minutes at 105°C (MOE recommended)

Other (please specify temperature and time):

_____

7. Instrumental Analysis

a) Light (C5-C10)

Instrument and Detector: _____

Column: _____

Injection Technique: _____

Quantification Standard: Toluene (MOE recommended) Other: _____

Integration range: Start of C5 to end of C10 (MOE recommended)

Other (please specify): _____

b) Extractables (Medium C10-C24 and Heavy C24-C50)

Instrument and Detector: _____

Column (please circle): OV-1ht, 30 m X 0.32 mm X 0.25 µm

DB-1ht, 30 m X 0.25 mm X 0.1 µm

Other (please specify) _____

Injection Technique: On column (MOE recommended)

Other (please specify): _____

Quantification Standard: C10-C24 C16 alkane (MOE recommended)

Other: _____

C24-C50 C36 alkane (MOE recommended)

Other: _____

Integration range: End of C10 to end of C24 (MOE recommended)

Other (please specify): _____

End of C24 to end of C50 (MOE recommended)

Other (please specify): _____

APPENDIX 3

TABLES OF METHODOLOGY INFORMATION SUMMARY

TABLE : AP1
LIGHT FRACTION METHODOLOGY INFORMATION SUMMARY

LABID	Weight	Sam.pretreatment	Instrument/detector	Column	Inj.tech	Quanti_std	Integ_range
98101	2-4g	None	P&T-MS	DB624	splitless	MOE-Recom.	MOE-Recom.
98102	1-2g	MeOH extraction	GC/MS	HP-5	Dirct couple	MOE-Recom.	MOE-Recom.
98103	5g		headspace/fid/pid	DB1		MOE-Recom.	MOE-Recom
98104	5g		GC/MS	DB624	P&T	MOE-Recom.	MOE-Recom.
98104A	10g		GC/FID	MXT-1	on column	gasoline standard	MOE-Recom.
98105	4g	shake in water 1hr.	GC/MS	DB624	P&T	MOE-Recom.	MOE-Recom.
98106	0.1-1.0g	heated	GC/MS	DB-VRX	P&T	MOE-Recom.	MOE-Recom.
98106A	2.5g	MeOH extraction	GC/MS	DB-VRX	P&T	MOE-Recom.	MOE-Recom.
98107	0.4-0.6g	None	GC/MS	VOCO	P&T	MOE-Recom.	MOE-Recom.
98107A	0.4-0.6g	None	GC/MS	VOCO	P&T	C7-C10	
98109	1g	none	GC/MS	DB624	P&T	MOE-Recom.	MOE-Recom.
98110A	0.1-0.2g	added int.std/water	GC/MS	SPB-5	P&T	MOE-Recom.	MOE-Recom.
98110B	2.2g	added int.std/water	Genesis headspace/fid	SPB-5	genesis sample loop	MOE-Recom.	MOE-Recom.
98112	1 g		GC/MS		P&T	MOE-Recom.	MOE-Recom.
98113	1 g	none	headspace GC/FID	DB624	direct conn.to headspace	MOE-Recom.	MOE-Recom
98114	1-2g		GC/FID	BTEX			

TABLE: AP 2
EXTRACTABLE MEDIUM AND HEAVY FRACTION METHODOLOGY INFORMATION SUMMARY
SAMPLE PREPARATION

LABID	Weight	Ext.tech	Ext.solvent	Backext	Cleanup Column	Cleanup-solvent
98101	5-6g	ultrasonic	hex/act(1:1)	yes	MOE-Procedure	40%dcm/hex
98102	5g	ultrasonic	hex/act(3:2)	no	silica gel clean-up in final extract	hexane
98103	5g	mechanical shaker	hex/act(1:1)	no	MOE-Procedure	40%dcm/hex
98104	10g	ultrasonic	hex/act(1:1)	yes	MOE-Procedure	40%dcm/hex
98104A	10g	ultrasonic	CS_2	no	Florisil	CS_2
98105	10g	shake-out	hex/act(1;1)	no	small amount of silica gel in extract	
98106	.5g	ultrasonic	hex/act(1:1)	yes	MOE-Procedure	40%dcm/hex
98106A	2.5g	ultrasonic	hex/act(1:1)	no	extract is silica treated, not thru column	hexane
98107	2.5-3g	ultrasonic	hex/act(1:1)	yes	MOE-Procedure	40%dcm/hex
98109	10g	soxhlet	hex/act(41:59)	yes	MOE-Procedure	hexane
98110	7g	Acc.solv.extracrtor	hex/act(4:1)	yes	1g silica gel shaken in a t-t	no
98112	6.5g	ASE	hex/act(3:1)	yes	silica gel addition&sonification	no
98113	10g	microwave	hex/act(1;1)	yes	yes	40%dcm/hex
98114	1-2g	ultrasonic	tetrachloroethylene/dichloromethylene	no	yes	no

TABLE: AP3
EXTRACTABLE MEDIUM AND HEAVY FRACTION METHODOLOGY INFORMATION SUMMARY
INSTRUMENTATION

LABID	Instrument/detector	Column	Inj.tech	Quant std C10_24	Quant std C24_50	Integ range _C10_24	integ range c24-50
98101	GC/FID-high temp	DB-1	MOE-Recom.	MOE-Recom.	MOE-Recom.	MOE-Recom.	MOE-Recom.
98102	CC/FID	HP-5	splitless	Diesel 20	NA	MOE-Recom.	
98103	GC/FID	DB-1	split/splitless	MOE-Recom.	MOE-Recom.	MOE-Recom.	MOE-Recom.
98104	GC/FID	MXT-1	MOE-Recom.	MOE-Recom.	MOE-Recom.	MOE-Recom.	MOE-Recom.
98104A	GC/FID	MXT-1	MOE-Recom.	Diesel Std	Diesel std	MOE-Recom.	MOE-Recom.
98105	GC/FID	HP5	Splitless	Diesel Fuel#2		MOE-Recom.	
98106	GC/FID		Splitless	MOE-Recom.	MOE-Recom.	MOE-Recom.	MOE-Recom.
98106A	GC/FID	DB-5	Splitless	MOE-Recom.	MOE-Recom.	MOE-Recom.	MOE-Recom.
98107	GC/FID	OV-1	split	MOE-Recom.	MOE-Recom.	MOE-Recom.	MOE-Recom.
98109	GC/FID	DB-1	split/splitless	MOE-Recom.	MOE-Recom.	MOE-Recom.	MOE-Recom.
98110	GC/FID	DBHT-SIM D	splitless	MOE-Recom.	MOE-Recom.	midpt10-midpt24	midpt24-midpt50
98112	GC/FID	RTX-5	splitless	MOE-Recom.	MOE-Recom.	MOE-Recom.	MOE-Recom.
98113	GC/FID	OV-1	MOE-Recom.	MOE-Recom.	MOE-Recom.	MOE-Recom.	MOE-Recom.
98114	GC/FID	DB-1	MOE-Recom.	Disel Standard.	mineral oil std	MOE-Recom.	IR?

TABLE: AP4
HEAVY OILS (GRAVIMETRIC) METHODOLOGY INFORMATION SUMMARY

LABID	Weight	Ext.vessel	Ext.tech	Ext.Solvent	Back ext	sample blow down (Y/N)	sample blowdown_describe	Cleanup_col	Cleanup-solvent	Drying Temp
98101	10-18g	Al.dish	ultrasonic	hex/act(1:1)	No	No		MOE-Procedure	No	MOE-Recom.
98102	5g	beaker	ultrasonic	hex/act(3:2)	no	yes	Rotovap at 40 deg	7cm SiO2	hexane	40 deg.,20 min
98103	5g	tube	soxhlet		no	yes		MOE-Procedure	MOE-Procedure	
98104	10g	Erlenmeyer flask	ultrasonic	hex/act(1:1)	yes	no		MOE-Procedure	MOE-Procedure	
98104A	10g	40ml capped vial	ultrsonic	CS2	no	no		Florisil	CS2	MOE-Recom.
98105	10g*	tube	shake-out	hex/act(1:1)	no	yes	n2 flow at 60 deg.	2g in large pipette tip	hexane only	104 deg for 60 min
98106	5g	tube	ultrasonic	hex/act(1:1)	yes	yes	Rotovap	MOE-Procedure	MOE-Procedure	MOE-Recom.
98106A	10g	rb flask	soxhlet	hex/act(1:1)	no	yes	Rotovap	Extract silica treated not thru column	hexane	rotovap 35deg
98106B	10g	rb flask	soxhlet	hex/act(1:1)	no	yes	Rotovap	Extract silica treated not thru colu	hexane	rotovap/105 deg 30 min
98107	2.5g	symbol	soxhlet	methylene chloride	yes	no		no	no	ambient temp-overnight,fumehood
98109	10g	soxhlet	soxhlet	hex/act(41:59)	yes	no	rotovap	MOE-Procedure	hexane	ambient temp,overnight,fumehood
98110	7g	Al.dish	Acc.solv.extractor							
98112	12g	tube	soxhlet	hexane	no	yes	fume hood at room temp	silica shake &filter	no	dryness at fume hood followed by 20 min at 70 deg
98113	5g	Beaker	Micro wave	hex/act(1:1)	yes	no		MOE-Procedure	40%DCM/HEXANE	dryness in fume hood
98114	1-2g (IR Tech.)	tube	ultrasonic	Methylene chloride	no	no		MOE-Procedure	Methylene chloride	

APPENDIX 4

LIST OF PARTICIPANTS

LIST OF PARTICIPANTS

(IN ALPHABETICAL ORDER)

1. Accutest Laboratories Ltd
2. Canviro Analytical Laboratories Ltd.
3. Entech, a division of Agri-Service Laboratory Inc.
4. Fisher Environmental Laboratories
5. Laboratory Services Branch, Ontario Ministry of the Environment
6. Lakefield Research Limited
7. Maxxam Analytics Inc.
8. Ontario Hydro
9. Philip Analytical Services, London
10. Philip Analytical Services, Mississauga
11. Philip Analytical Services, Burlington
12. Water Technology International Corporation